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AGENCY USE ONLY (Leave blank)	2. REPORT DATE 30 November 200	3. REPORT TYPE A		S COVERED - 31 May 00	
4. TITLE AND SUBTITLE Do Electrons or Holes Activate Molecular 02 on TiO2 Surfaces?				AG55-97-1-0169	
6. AUTHOR(S) John T. Yates, Jr.					
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES) University of Pittsburgh Department of Chemistry Pittsburgh, PA 15260				FORMING ORGANIZATION DRT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING / MONITORING AGENCY REPORT NUMBER		
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				O 36939.5-CH-AAS	
11. SUPPLEMENTARY NOTES			1		
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12a. DISTRIBUTION / AVAILABILITY STATEMENT			12 b. DISTRIBUTION CODE		
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13. ABSTRACT (Maximum 200 words)					
See page 1 and 2 of report					
ENC CUALITY EVILLED 4					
20010116 141					
14. SUBJECT TERMS platinum, oxygen, defect sites, photochemistry, 3					
photodissociation, photodesorption, carbon single walled nanotubes, oxidation, 0, nanotube defect sites, adsorption				16. PRICE CODE	
nanotubes 17. SECURITY CLASSIFICATION 18. SECURITY CLASSIFICATION 19. SECURITY CLASSIFICATION 20. LIMITATION OF ABSTR					
OR REPORT UNCLASSIFIED	OF THIS PAGE UNCLASSIFIED	OF ABSTRACT UNCLASSIFIE		UL	

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Sincerely,

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Enclosure 3

Do Electrons or Holes Activate Molecular O2 on TiO2 Surfaces?

Final Report

John T. Yates, Jr.

30 November 2000

U.S. ARMY RESEARCH OFFICE

DAAG55-97-1-0169

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FINAL REPORT

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- 1. ARO PROPOSAL NUMBER: 36939-CH-AAS
- 2. **PERIOD COVERED BY REPORT:** June 1997 May 2000
- 3. TITLE OF PROPOSAL: Do Electrons or Holes Activate Molecular O₂ on TiO₂ Surfaces?
- 4. CONTRACT OR GRANT NUMBER: DAAG55-97-1-0169
- 5. NAME OF INSTITUTION: University of Pittsburgh
- 6. **AUTHOR OF REPORT:** John T. Yates, Jr.
- 7. LIST OF MANUSCRIPTS SUBMITTED OR PUBLISHED UNDER ARO SPONSORSHIP:
 - "Comparison of Thermal and Photochemical Behavior of O₂ Chemisorbed on Pt(335)." D. V. Heyd, R. J. Scharff and J. T. Yates, Jr. J. Chem. Phys. 110, 6939 (1999).

The thermal and photochemical behavior of O₂ chemisorbed on a stepped Pt(335) surface have been compared using temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS). Molecular O₂ adsorbs preferentially at 85 K on step sites, followed by adsorption on terrace sites. On heating below 250 K, depopulation of terrace sites occurs first followed by depopulation of step sites. Both desorption and dissociation of O₂(a) occur below 250 K. Photolysis of O₂ occurs preferentially on step sites, with a cross section $\approx 3 \times 10^{-21}$ cm². The chemisorbed O(a) produced by either thermal dissociation or photodissociation of O₂(a) is identical, exhibiting a Pt-O stretching mode at 480 cm⁻¹ and a frustrated translation mode at 330-350 cm⁻¹. Two regimes of photodepletion are observed, dominated by photolysis of step bound-O₂ (regime I) and of terrace bound-O₂ (regime II). Regime II is characterized by the presence of interactions of photoproduced electronegative O(a) with remaining $O_2(a)$, causing an increase of the O-O mode frequency due to electron withdrawal from the $O_2(a)$ π^* orbital.

2. "Infrared Spectral Evidence for the Etching of Carbon Nanotubes: Ozone Oxidation at 298 K." Douglas B. Mawhinney, Viktor Naumenko, Anya Kuznetsova, John T. Yates, Jr., J. Liu and R. E. Smalley, J. Am. Chem. Soc. 122, 2383 (2000).

We have employed infrared spectroscopy to monitor the reaction of O₃ with single walled carbon nanotubes. Ester and quinone groups are produced, as well as gas phase CO and CO₂. The rate of formation of these species decreases at higher O₃ exposures as active sites are consumed. The O₃-derived functional groups may be removed as CO₂ gas by heating in vacuum to 873 K, leaving the carbon nanotube walls intact.

3. "Enhancement of Adsorption Inside of Single-Walled Nanotubes: Opening the Entry Ports." Anya Kuznetsova, Douglas B. Mawhinney, Viktor Naumenko, John T. Yates, Jr., J. Liu and R. E. Smalley, *Chem. Phys. Lett.* 321, 292 (2000).

Opening the ends of the single-walled carbon nanotube by thermal activation increases both the kinetic rate and the saturation capacity of the nanotubes for Xe adsorption at 95 K. Infrared studies show the existence of carboxylic acid and quinone groups on the nanotube surface prior to heating above 623 K. These groups decompose during heat treatment of the nanotube sample from 623 to 1073 K producing CO, CO₂, CH₄ and H₂. The removal of a large number of these groups opens the entry ports for adsorption on the inner surface of the nanotube and leads to dramatically enhanced Xe adsorption.

4. "Surface Defect Site Density on Single Walled Carbon Nanotubes by Titration." Douglas B. Mawhinney, Viktor Naumenko, Anya Kuznetsova, John T. Yates, Jr., J. Liu and R.E. Smalley, *Chem. Phys. Lett.* **324**, 213 (2000).

Closed end single walled carbon nanotubes (c-SWNT) purified by acidic oxidation have been studied in order to determine the fraction of oxidized carbon sites present. This has been done by measuring the evolution of $CO_2(g)$ and CO(g) on heating to 1273 K. Following a 1273 K treatment, the defect sites were titrated repeatedly with O_3 . The results indicate that $\sim 5\%$ of the carbon atoms in the c-SWNT samples pretreated to 1273 K are located at defective sites, capable of facile oxidation by O_3 . This high defect site density indicates that a significant number of these sites exist on the graphene walls of the nanotubes.

8. SCIENTIFIC PERSONNEL:

Mr. R. Jason Scharff, M.S. Dr. Douglas B. Mawhinney, Ph.D.

9. REPORT OF INVENTIONS:

The discovery of a method to enhance adsorption inside of single walled nanotubes by thermal activation, removing blocking functional groups at the entry ports to the interior, is the subject of a patent application which is being processed at the U. S. Patent Office.

10. Brief Review of Research Findings

A. OXYGEN PHOTOCHEMISTRY ON SURFACES

This project began with the study of the photochemistry of O_2 chemisorbed on a stepped Pt single crystal surface. The study found that photolysis of O_2 occurred primarily on step sites and that both photodissociation and photodesorption occur together. The experiments compared thermal dissociation of O_2 and photodissociation. In both cases the O_2 molecules were more rapidly depleted on the step sites than on the terrace sites.

ASSERT Student: Mr. R. Jason Scharff

B. NANOTUBE CHEMISTRY

Because of the great interest in nanotubes, our attention then turned to this topic. We were the first to employ infrared spectroscopy to observe the chemistry of the nanotubes under oxidizing conditions, observing the production of specific organic moieties by oxidation. The thermal stability of these groups was studied by infrared spectroscopy, and their conversion into CO and CO₂ was monitored. We pioneered the use of ozone as an oxidizing agent to probe the defect sites on the nanotube surface, finding that nanotubes which have been treated in HNO₃ to remove impurities are defective to about the 5% level. Removal of these defect sites opens the entry ports into the nanotube interior, causing the kinetics of adsorption of a test molecule, Xe, to be markedly enhanced.

ASSERT Student: Dr. Douglas B. Mawhinney